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O. V. Krylov, Yu. Ye. Sinyak, A. A. Berlinn and I. L. Shul'gina

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KINETICS AND CATALYSTS OF FORMALDEHYDE CONDENSATION

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ABSTRACT: This paper describes comparative tests on the kinetics of formaldehyde condensation in the presence of certain quantities of $Ca(OH)_2$ and after filtration of solid precipitate formed by adding $Ca(OH)_2$ to the mixture. These tests indicate that the condensation of formaldehyde to sugars is homogeneous. The effect of formaldehyde and sugars on the solubility of $Ca(OH)_2$ is examined. It is concluded that the reaction of CH_2O condensation proceeds through the intermediate formation of triose and as a triose then forms a complex with the Ca ion leading to further condensation. The catalytic activity of the hydroxides of the rare earth metals in the synthesis of carbohydrates from formaldehyde, though lower than that of the hydroxides of Ca, Sr, Ba, Pb, Tl, is higher than all other compounds tested. Comparison of pH data indicates that the conversion of formaldehyde by the Cannizzaro reaction is negligible in the presence of lanthanoid hydroxide and that the selectivity of the process of monosaccharide synthesis from CH_2O is substantially higher than in the presence of $Ca(OH)_2$. The investigation verifies the hypothesis that ion radius plays a deciding role in the manifestation of catalytic activity in the condensation of formaldehyde into to monosaccharide.

INTRODUCTION

Earlier we analyzed the transition of formaldehyde in monosaccharides /643* [1-3]:

$$CH_2O \rightarrow C_n(H_2O)_n,$$

where n = 5 or 6. The reaction proceeds in aqueous solutions in the presence of catalysts--hydroxides of alkali or metals. The reaction kinetics at 25--60° C are described by the autocatalysis equation:

$$-d[CH_2O] / dt = k[Ca(OH)_2] [CH_2O] [Pr],$$

*Numbers in the margin indicate foreign pagination.

where [Pr] are the reaction products (of monosaccharide); the activation energy for $Ca(OH)_2$ is 11.3 kilocalorie/mole, and for $Sr(OH)_2$ 12.2 kilocalorie/mole [2].

Examination of the reaction rate as a function of formaldehyde concentration reveals that only up to 0.5% CH_2O in solution is the reaction rate a linear function of $[CH_2O]$; in the interval of 2.5-10% CH_2O, however, the reaction rate is not a function of $[CH_2O]$. Tests on the artificial addition of various monosaccharides to the initial reaction mixture have shown that the dependence of the reaction rate on the co-catalysts concentration is also nonlinear [3]. On the basis of these data we may write, instead of (1) the Langmuir type equation:

$$-\frac{d[CH_2O]}{dt} = k[Ca(OH)_2]\frac{b[CH_2O]}{1+b[CH_2O]}\frac{b'[Pr]}{1+b'[Pr]}$$

At higher CH_2O and co-catalysts concentrations equation (2) becomes

$$-d[CH_2O]/dt = k[Ca(OH)_2].$$

Equation (3) was also experimentally observed in the simultaneous but independent studies of Weiss, La Pierre and Shapira [4]. The corresponding conversion shows that their constant k = 3.5 min^{-1} at 60° is approximately one half our value. These authors also analyzed the kinetics of the Cannizzaro reaction that proceeds in the presence of $Ca(OH)_2$ according to the equation

$$4CH_2O + Ca(OH)_2 \rightleftarrows (HCOO)_2Ca + 2CH_3OH.$$

Its kinetics corresponds to the equation

$$-d[CH_2O]/dt = k_1[Ca(OH)_2][CH_2O],$$

which differs from equation (3) of sugar synthesis. The apparent deviations of dependents (3) from linearity at low $Ca(OH)_2$ concentrations were attributed to the consumption of $Ca(OH)_2$ by the Cannizzaro reaction. In this case $Ca(OH)_2$ is consumed in the formation of salt. When the initial concentration of $Ca(OH)_2$ is less than 0.02 mole per litre the condensation of formaldehyde, according to published data [4] and according to our data, does not take place at all.

We conducted comparative tests on the condensation kinetics of formaldehyde: 1) in the presence of a certain quantity of $Ca(OH)_2$ (1-2 gram per 100 milliliter of 4% CH_2O solution) and 2) after filtration of the solid precipitates formed by adding $Ca(OH)_2$ to the mixture. The kinetic curves of CH_2O consumption coincided in both cases, and the percent of conversion of formaldehyde to sugar was higher in the second case, indicating the decomposition of sugar in the presence of alkali. /644

These tests indicate that the condensation of formaldehyde into sugars is a homogeneous reaction. Special tests also demonstrated that the solubility of $Ca(OH)_2$ is considerably higher in the presence of formaldehyde and sugars. Only when the concentration of CH_2O in the solution is higher than 10% does the solubility of $Ca(OH)_2$ decrease; this is apparently the result of the reduction of the reaction rate at CH_2O concentrations higher than 10%, a fact that we noted earlier [2].

On the basis of these tests, obviously, equation (2), which resembles the equation of heterogeneous catalyst reactions, can be explained by chelation of the Ca ion with the formaldehyde and reaction products--monosaccharide, and by the condensation reaction in the coordination sphere. The constants b and b', analogist to the absorption coefficients are in this case the chelation equilibrium constants. Considering the data in [5] on the nuclear magnetic resinous spectra of the complexes of different metal ions with sugars and our data on the ultraviolet spectra of complexes, we propose the formation of comparatively unstable complexes, in which the hydrogen atom in the OH-group of monosaccharide is not substituted for the metal.

The rate constant of condensation of formaldehyde in the presence of $Ca(OH)_2$ without a co-catalyst, or more accurately the product of the constants kb' [2] can substantially exceed the value of kb' after the addition of co-catalysts--carbohydrates [3], to the mixture. Only the addition of triose-glycerinaldehyde makes the value of kb' close to kb' without a co-catalyst. Hence it can be concluded that the reaction of CH_2O proceeds through the intermediate formation of triose and that the triose then forms a complex with the Ca ion, leading to further condensation. Actually, we detected triose with the aid of paper chromatography. Complexes with pentose and hexose are less active. It has been

suggested [4] that their accellerating action is caused by partial equilibrium decomposition to lower carbohydrates--triose and glycolaldehyde.

In contrast to formaldehyde condensation, the Cannizzaro reaction proceeds by the mechanism of alkaline catalysts and the intermediate complex contains not metal ions but the OH-ion [4].

In addition to the compounds of alkali earth metals, the compounds of thallium [6] and lead [7] are also catalytically active in the synthesis of carbohydrates from formaldehyde. These ions, according to published data [5], form complexes with sugars, similar with respect to properties to complexes of alkali earth metals. New catalysts for the synthesis of carbohydrates obviously should also be looked for among metal compounds, the chelating properties of whose ions are close to the properties of the above mentioned metals.

Excluding the alkali metals, whose hydroxides in aqueous solutions convert formaldehyde according to the Cannizzaro reaction, then with respect to ion radius the rare earth elements are closest to the above stated ions. According to Pauling [8], the ion radius of the latter varied from 0.99 to 1.18 Ångstroms. For chelate complexes, which can be formed under the conditions of carbohydrate synthesis, the presence of a sufficiently large ion makes it possible to accomodate a large number of ligands. It is known [9] that the lanthanide complexes are characterized by coordination numbers 9 and 10.

Our tests show that hydroxides of the rare earth metals, although inferior to the hydroxides of calcium, strontium, berium, lead and thallium with respect /645
to catalytic activity, are nevertheless superior to all other elements which we tested. At 80-110° they converted formaldehyde to sugars at a satisfactory rate. Glucose, fructose, rhamnose and ribose were identified in the reaction products by paper chromatography. Under the standard test conditions used by us, (110° in an autoclave, 100 millileter of 4% of CH_2O solution and 2 grams of catalyst) the process proceeded to 100% consumption of formaldehyde in 5-6 hours. The kinetics of conversion of CH_2O corresponded to the kinetics of condensation of CH_2O to $Ca(OH)_2$ and $Sr(OH)_2$ [2], i.e. auto catalytic (Figure 1,1). The induction period lasted 3 to 4 hours. The use of co-catalysts--glucose, as in the case of previously tested catalysts, shortened or completely eliminated the induction period.

In terms of catalytic activity (rate constant of CH_2O condensation) the hydroxides of La, Tb, Ho, Tu, Gd, Dy, Er, Sm which we tested, and also $Y(OH)_3$ differ by no more than 20-30%. $Eu(OH)_3$ was somewhat less active.

The investigated hydroxides are characterized by the fact that the reaction proceeds in acidic solutions. At 80° the pH of the solution dropped from 6.3 to 6.0 during the reaction time, and at 110°, from 1.3 to 4.8. These figures show that the conversion of formaldehyde by the Cannizzaro reaction is negligible in the presence of lanthanoid hydroxides and that, consequently, the selectivity of the process of monosaccharide synthesis from CH_2O is considerably greater than in the presence of $Ca(OH)_2$. The ions coordinate large numbers of molecules in an acidic medium.

The hydroxides of other trivalent ions which we tested, the radii which were less than 1.0 Angstrom: $Sc(OH)_3$, $Al(OH)_3$, $B(OH)_3$, $In(OH)_3$, $Ga(OH)_3$ in the investigated temperature range (25-110°) were catalytically inactive.

The hydroxides of the tetravalent ions with about the same radii ($Ce(OH)_4$ and $Th(OH)_4$) catalyzed the conversion of formaldehyde at 80-110°, although much of it reacted according to the Cannizzaro reaction. Thus at 110° with the same concentrations of reagents in the presence of $Ce(OH)_4$, formaldehyde disappeared after 9 hours, and the pH dropped from 5.5 to 2.5; in the presence of $Th(OH)_4$ the reaction took 7 hours and the pH dropped from 4.6 to 2.8. The reaction proceeded without an induction period (Figure 1 and 2). Paper chromatography indicated the presence of triose, but not of hexose in the reaction product.

Thus the investigation described here verified the hypothesis that the radius of the ion is of deciding importance with respect to its catalytic activity in the condensation of formaldehyde to monosaccharides.

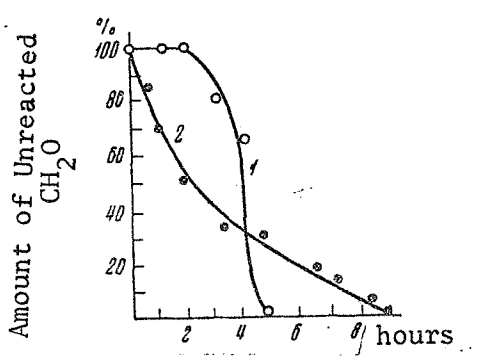

Figure 1: Kinetic Curves of Consumption of Formaldehyde at 110°C in the Presence of Catalysts: 1. $Sm(OH)_3$; 2. $Ce(OH)_4$

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